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(54) Title of the invention

Hardening Composite

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(72) Inventor

Arakawa Tsukasa

Kanagawa ken, Kawasaki shi, Kawasaki ku,  
Chidori cho, 3 - 2.

Showa Denko Kabushiki Kaisha Kawasaki  
Juki Kenkyusho Nai

(Internal to Kawasaki Resin Research Center  
of Showa Electrical Co. Ltd.)

(72) Inventor

Maruyama Satoshi

Kanagawa ken, Kawasaki shi, Kawasaki ku,  
Chidori cho, 3 - 2.

Showa Denko Kabushiki Kaisha Kawasaki  
Juki Kenkyusho Nai

(Internal to Kawasaki Resin Research Center  
of Showa Electrical Co. Ltd.)

(72) Inventor

Yoshida Haruo

Oita ken, Oita shi, Oji Nakanoshu, 2.

Showa Denko Kabushiki Kaisha Oita

(72) Inventor

Kenkyusho Nai

(Internal to Oita Research Center of Showa  
Electrical Co. Ltd.)

Tatsuke Hiroyuki

Oita ken, Oita shi, Oji Nakanoshu, 2.

Showa Denko Kabushiki Kaisha Oita  
Kenkyusho Nai

(Internal to Oita Research Center of Showa  
Electrical Co. Ltd.)

(71) Patent Applicant

Showa Denko Kabushiki Kaisha

(Showa Electrical Co. Ltd.)

Tokyo to, Minato ku, Shibataiseki, 1 cho me,  
13 ban, 9 go.

(74) Representative

Patent Attorney Kikuchi Seiichi

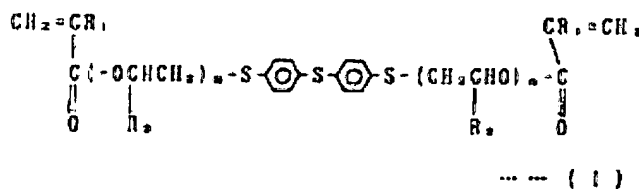
## A Detailed Description

### 1. Title of the invention

Hardening Composite.

### 2. Scope of patent claims

The hardening composite that is formed from monomer component formed from 10 ~ 100 weight % of 4, 4' - bis [ $\omega$  - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound shown by the general formula (1) given below and 90 ~ 0 weight % of vinyl group monomer copolymerizable with this compound, and radical polymerization initiator.



(Wherein,  $\text{R}_1$  and  $\text{R}_2$  independently show hydrogen or methyl radical and  $m$  and  $n$  are integers from 1 ~ 5.)

### 3. Detailed description of the invention

#### [Industrial applicability]

The present invention relates to hardening composite. In further details, the present invention relates to the hardening composite that has the characteristic of containing 4, 4' - bis [ $\omega$  - (metha)

acryloyl (polyoxy alkylene) thio] phenyl sulfide compound. The hardening composite of the present invention has excellent hardening property and hardened material obtained by hardening this hardening composite has high refractive index and moreover, has excellent heat resistance, low water absorbance and optical evenness due to which it is extremely useful in industrial fields like optical material, coating agent, sealing agent, paint, adhesive etc. and it is particularly useful in the field of optical material.

#### **[Techniques of the past]**

Polymers such as polystyrene group resins, poly methyl methacrylate group resins, polycarbonate resins, di ethylene glycol di allyl carbonate are used as organic optical material since past and their demand is rising due to their lightweight, safety, excellent operability and dyeing property.

However, the organic optical material of the past such as poly methyl methacrylate group resin, has high moisture absorbing property as the resin property and as a result of moisture absorption, its shape and refractive index changes and it becomes unstable as optical material. Moreover, polystyrene group resin and polycarbonate resin have the disadvantage of generation of optical birefringence (double refraction), scattered light, lowering of transparency due to temporal change etc. Furthermore, di ethylene glycol di allyl carbonate polymer has limited application scope as optical material due to low refractive index (refractive index = 1.499).

Different resins used for optical material have been proposed in order to reform these disadvantages. As examples, Patent number Sho 57 – 28115, Sho 57 – 28116, Sho 59 – 184210, Sho 60 – 7314, Sho 60 – 179406, Sho 60 – 217301, Sho 60 – 186514, Sho 60 – 166307, Sho – 103301, Sho 60 – 124607, Sho 62 – 232414, Sho 62 – 235901, Sho 62 – 267316, Sho 63 - 15811, Sho 63 – 46213, Sho 63 – 72707 etc. can be given.

However, these composites obtained by the technique of past are optically uneven, under coloration, lack dimension stability due to which these cannot be used as optical material.

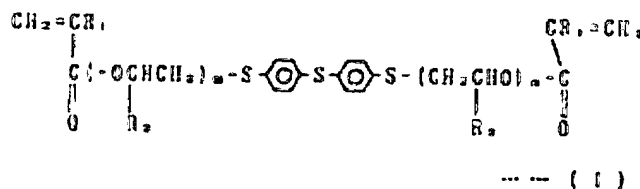
#### **[Problems the invention solves]**

The present invention aims at subjugating the problems of the resin used for optical material of the past and offers a hardening composite suitable for use in the manufacture of hardened material having balance between properties such as optical evenness, low water absorbance, heat resistance, that can also be used as material of coating agent, sealing agent, paint, adhesive etc.

#### **[Method to solve the problems]**

The present invention offers the hardening composite that achieves the aim mentioned above. Namely, the present invention offers the hardening composite that is formed from monomer component formed from 10 ~ 100 weight % of 4, 4' – bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound shown by the general formula (1) given below and 90 ~ 0 weight %

of vinyl group monomer copolymerizable with this compound, and radical polymerization initiator.



(Wherein, R<sub>1</sub> and R<sub>2</sub> independently show hydrogen or methyl radical and m and n are integers from 1 ~ 5.)

The 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound shown by the general formula (1) given above used in the present invention can be easily synthesized by carrying out hydroxy alkylation by reacting 4, 4' - di mercapto phenyl sulfide and ethylene oxide or propylene oxide using base such as sodium hydroxide and then carrying out esterification reaction with (metha) acrylic acid.

Moreover, as regards the another manufacturing method of 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound shown by the general formula (1) given above, the method of carrying out hydroxy alkylation by reacting 4, 4' - di mercapto phenyl sulfide and ethylene carbon or propylene carbonate using potassium carbonate as catalyst and then carrying out esterification reaction with (metha) acrylic acid, can be given.

The 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound shown by the general formula (1) given above has the merit of being easily mixable with vinyl group monomer copolymerizable with it and having low affinity towards water and moreover, having high refractive index. Therefore, properties of hardened material obtained by hardening the hardening composite can be changed by mixing at least 1 type of 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound with vinyl group monomer copolymerizable with it with desired blending ratio as per the usage.

The usage quantity of 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound used in the present invention should be at least 10 weight %, desirably at least 15 weight % in the total quantity of monomer component and 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound can be independently polymerized.

If the usage quantity of 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound is less than 10 weight %, then optical property, water absorbance and heat resistance of the hardened material obtained by hardening become insufficient. The usage quantity of 4, 4' - bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound can be freely changed between the range from 10 ~ 100 weight % corresponding to the usage and type of vinyl group monomer copolymerizable with this compound.

For example, in order to increase the refractive index and heat resistance of the hardened material and lower the water absorbance, blending quantity of 4, 4' – bis [ $\omega$  - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound can be increased.

The copolymerizable vinyl group monomer used in the present invention can be mono-functional or multifunctional and it should be compatibility with 4, 4' – bis [ $\omega$  - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound. Moreover, 2 or more than 2 types of copolymerizable vinyl group monomer can be used by mixing.

As regards the vinyl group monomer copolymerizable with 4, 4' – bis [ $\omega$  - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound, unsaturated fatty acid ester, aromatic vinyl compound, unsaturated fatty acids and their derivatives, unsaturated dibasic acid and their derivatives, vinyl cyanide compounds such as (metha) acrylonitrile etc. can be given.

As regards the unsaturated fatty acid ester, alkyl (metha) acrylate such as methyl (metha) acrylate, ethyl (metha) acrylate, butyl (metha) acrylate, 2 – ethyl hexyl (metha) acrylate, octyl (metha) acrylate, do decyl (metha) acrylate, octa decyl (metha) acrylate, cyclo hexyl (metha) acrylate, methyl cyclo hexyl (metha) acrylate, (iso) volnyl (?) (metha) acrylate, adamantyl (metha) acrylate etc., acrylic acid aromatic ester such as phenyl (metha) acrylate, benzyl (metha) acrylate, 1 – naphthyl (metha) acrylate, fluoro phenyl (metha) acrylate, chloro phenyl (metha) acrylate, bromo phenyl (metha) acrylate, tri bromo phenyl (metha) acrylate, methoxy phenyl (metha) acrylate, cyano phenyl (metha) acrylate, bi phenyl (metha) acrylate, bromo benzyl (metha) acrylate etc., halo alkyl (metha) acrylate, fluoro methyl (metha) acrylate, chloro methyl (metha) acrylate, bromo ethyl (metha) acrylate, tri chloro methyl (metha) acrylate etc., 2 – hydroxy ethyl (metha) acrylate, (metha) acrylic acid polyethylene glycol ester etc., (metha) acrylic acid ester such as glycidyl (metha) acrylate, alkyl amino (metha) acrylate etc. can be given. Moreover,  $\alpha$  - substituted acrylic acid ester such as  $\alpha$  - fluoro acrylic acid ester,  $\alpha$  - cyano acrylic acid ester etc. can be given.

As regards the aromatic vinyl compound, styrene,  $\alpha$  - substituted styrene such as  $\alpha$  - methyl styrene,  $\alpha$  - ethyl styrene,  $\alpha$  - chloro styrene etc., nuclear substituted styrene such as fluoro styrene, chloro styrene, bromo styrene, chloro methyl styrene, methoxy styrene etc. can be given.

As regards the unsaturated fatty acids and their derivatives, (metha) acrylamides such as (metha) acrylamide, N, N – di methyl (metha) acrylamide, N, N – di ethyl (metha) acrylamide etc., (metha) acrylic acid etc. can be given.

As regards the unsaturated dibasic acids and their derivatives, N – substituted maleimide such as N – methyl maleimide, N – ethyl maleimide, N – butyl maleimide, N – cyclo hexyl maleimide, N – phenyl maleimide, N – methyl phenyl maleimide, N – chloro phenyl maleimide, N – carboxyl phenyl maleimide etc., maleic acid, anhydrous maleic acid, fumaric acid etc. can be given.

As regards the copolymerizable vinyl group monomer other than uni-functional vinyl unimers mentioned above, bridging multifunctional monomer can be given. For example, di (metha) acrylate such as ethylene glycol di (metha) acrylate, di ethylene glycol di (metha) acrylate, tri ethylene glycol di (metha) acrylate, tetra ethylene glycol di (metha) acrylate, tri propylene glycol di (metha) acrylate, 1, 2 – butylene glycol di (metha) acrylate, 1, 4 – butane diol di (metha) acrylate, 1, 5 – pentadiol di (metha) acrylate, 1, 6 – hexane diol di (metha) acrylate, neo pentyl glycol di (metha) acrylate, hydroxy pivalic acid neo pentyl glycol ester di (metha) acrylate, oligoester di (metha) acrylate, poly butadiene di (metha) acrylate, 2, 2 – bis (4 – (metha) acryloyloxy phenyl) propane, 2, 2 – bis (4 – (ω - (metha) acryloyloxy poly ethoxy)phenyl) propane, 2, 2 – bis (4 – (ω - (metha) acryloyloxy poly ethoxy) di bromo phenyl) propane, 2, 2 – bis (4 – (ω - (metha) acryloyloxy poly ethoxy)phenyl) propane, bis (4 – (ω - (metha) acryloyloxy poly ethoxy)phenyl) methane etc., bifunctional bridging monomer such as di allyl phthalate, di allyl iso phthalate, di allyl terephthalate, di allyl carbonate, di ethylene glycol di allyl carbonate, di vinyl benzene, N, N' – m – phenylene bis maleimide etc., tri-functional bridging monomer such as tri methylol ethane tri (metha) acrylate, tri methylol propane tri (metha) acrylate, penta erythritol tri (metha) acrylate, tri (metha) allyl is cyanurate, tri allyl tri meritate (?), di allyl chlorindate (?) etc., quadri-functional bridging monomer such as penta erythritol tetra (metha) acrylate etc. can be given.

The composite of 4, 4' – bis [ω - (metha) acryloyl (polyoxy alkylene) thio] phenyl sulfide compound and copolymerizable vinyl group monomer can be hardened by radical polymerization. The radical polymerization initiator used in radical polymerization can be any radical polymerization initiator that can generate radical by heat, microwaves, infrared rays or ultraviolet rays and it can be chosen as per the application of hardening composite and purpose.

As regards the radical polymerization initiator that can be used at the time of carrying out polymerization by heat, microwaves and infrared rays, azo group compound such as 2, 2' - azo bis iso butylnitrile, 2, 2' - azo bis iso valeronitrile (?), 2, 2' - azo bis (2, 4 – di methyl valeronitrile (?)) etc., ketone peroxide such as methyl ethyl ketone peroxide, methyl iso butyl ketone peroxide, cyclo hexanone peroxide, acetyl acetone peroxide etc., di acyl peroxide such as iso butyl peroxide, 2, 4 – di chloro benzoyl peroxide, o – methyl benzoyl peroxide, lauroyl peroxide, p – chloro benzoyl peroxide etc., hydro peroxide such as 2, 4, 4 – tri methyl pentyl – 2 – hydro peroxide, di iso propyl benzene peroxide, cumene hydro peroxide, t – butyl peroxide etc., di alkyl peroxide such as di cumyl peroxide, t – butyl cumyl peroxide, di – t – butyl peroxide, tris (t – butyl peroxy) tri azine etc., peroxy ketal such as 1, 1 – di – t – butyl peroxy cyclo hexane, 2, 2 – di (t – butyl peroxy) butane etc., alkyl per ester such as t – butyl peroxy pivalate, t – butyl peroxy – 2 – ethyl hexanoate, t – butyl peroxy iso butylate, di - t – butyl peroxy hexa hydro terephthalate, di - t – butyl peroxy azelate, t – butyl peroxy – 3, 5, 5 – tri methyl hexanoate, t – butyl peroxy acetate, t – butyl

peroxy benzoate, di - t - butyl peroxy tri methyl adipate etc., per carbonate such as di iso propyl peroxy di carbonate, di - sec - butyl peroxy di carbonate, t - butyl peroxy di carbonate etc. can be given.

As regards the radical polymerization initiator that can be used at the time of carrying out polymerization by ultraviolet rays, carbonyl compound such as acetophenone, 2, 2 - di methoxy - 2 - phenyl acetophenone, 2, 2 - di ethoxy acetophenone, 4' - iso propyl - 2 - hydroxy - 2 - methyl propiophenone, 2 - hydroxy - 2 - methyl propiophenone, 4, 4' - bis (di ethyl amino) benzophenone, benzophenone, methyl (o - benzoyl) benzoate, 1 - phenyl 1, 2 - propane dion - 2 - (o - ethoxy carbonyl) oxime, 1 - phenyl - 1, 2 - propane dion - 2 - (o - benzoyl) oxime, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin iso propyl ether, benzoin iso butyl ether, benzoin octyl ether, benzyl, benzyl di methyl ketal, benzyl di ethyl ketal, di acetyl etc., anthraquinone or thio xanthone derivative such as methyl anthraquinone, chloro anthraquinone, chloro thio xanthone, 2 - methyl thio xanthone, 2 - iso propyl thio xanthone etc., sulfur compounds such as di phenyl di sulfide, di thio carbamate etc. can be given.

The usage quantity of radical polymerization initiator changes with the type of radical polymerization initiator, type and composition ratio of monomer, however, it should be within the range from 0.001 ~ 20 mole %, desirably 0.01 ~ 10 mole % with respect to monomer component. If the usage quantity of radical polymerization initiator is less than 0.001 mole %, polymerization requires long time whereas if it is more than 20 mole %, then it is not only uneconomical, but bubbles are generated during the polymerization and molecular weight of the hardened material obtained by polymerization remarkably reduces which is not desired.

The hardening composite of the present invention can be polymerized and hardened as it is or it can be preparatory polymerized and then polymerization and hardening is carried out based on which viscosity can be regulated and shrinkage ratio at the time of polymerization can be reduced.

The hardening composite of the present invention can be used by blending with different fillers as per requirement when light permeability is not particularly required. As regards the filler, glass fibers, alumina fibers, carbon fibers, aramid fibers, powder fillers such as silica, alumina, barium sulfate, titanium oxide etc. can be given. Other than these, flame retardation material, dye, pigment etc. can also be used jointly.

The polymerization temperature and polymerization time at the time of hardening the hardening composite differ with the type and usage quantity of the used radical polymerization initiator, however, polymerization temperature is desired to be within the range from 0 ~ 200°C and polymerization time is desired to be within the range from 0.5 ~ 50 hours.

#### **[Practical examples]**

The present invention has been explained below in further details with the help of practical

examples and comparative examples.

Moreover, properties of hardened material obtained in practical examples and comparative examples were measured by following methods.

(1) Refractive index

Refractive index was measured at 20°C by using Abbe refractometer (Shimazu Seisakujo make 3L model).

(2) Light permeability

Permeability of 3 mm thick flat plate was measured by light having wavelength of 550 nm by using spectrophotometer (Hitachi Seisakujo make 150 – 20 model).

(3) Glass transition temperature (T<sub>g</sub>)

Glass transition temperature of the specimen (thickness 0.1 mm) was measured by taking the readings from peak of tan δ (point of inflection) using viscoelasticity measuring device (Orientech make Leopypron DDV – II – EP model).

(4) Water absorbance

Test plate of JIS – K – 7209 was used and proportion of increase in weight at the time of soaking the sample dried under reduced pressure at 50°C for 5 days, in water of 100°C for 2 hours, against dry weight was measured.

**(Practical example 1)**

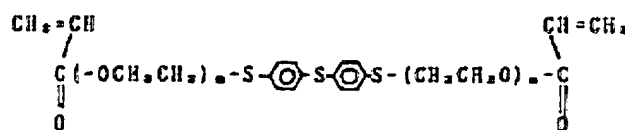
250 mg of 2, 2' – azo bis (2, 4 – di methyl valeronitrile) taken as radical polymerization initiator was dissolved in 50 g of 4, 4' – bis (2 – acryloyloxy ethyl thio) phenyl sulfide (polymerizable monomer A) and it was injected in glass mold of 5 cm x 5 cm x 0.3 cm and glass cell of 0.2 mm x 50 mm x 20 mm respectively and heating was carried out at 35°C under nitrogen current for 10 hours after which it was heated up to 80°C with the rate of rise of temperature of 10°C/hr and the mold was released and hardening was further carried out by heating at 100°C for 1 hour.

The obtained hardened material was a homogeneous colorless transparent resin. The property values of the hardened material have been given in table 1.

**(Practical example 2)**

Polymerizable monomer B

The compound shown by the formula given below was hardened by the procedure similar to practical example 1.



(mixture of m + n = 4 – 6)

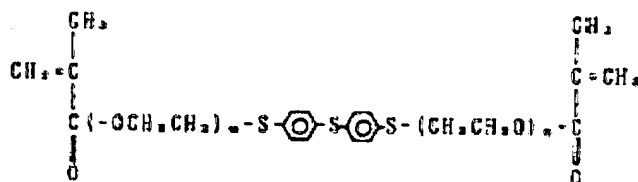


The property values of the obtained hardened material have been given in table 1.

**(Practical example 3)**

Polymerizable monomer C

The compound shown by the formula given below was hardened by the procedure similar to practical example 1.



(mixture of  $m + n = 2 - 6$ )

The property values of the obtained hardened material have been given in table 1.

**(Practical example 4)**

4, 4' - bis (2 - acryloyloxy propyl thio) phenyl sulfide (polymerizable monomer D) was hardened by the procedure similar to practical example 1. The property values of the obtained hardened material have been given in table 1.

**(Practical examples 1 ~ 3 and comparative examples 1 ~ 3)**

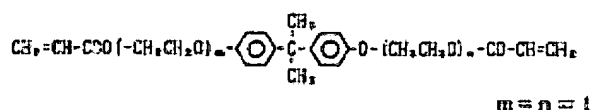
Other vinyl group monomer was mixed with the polymerizable monomer A, B and C shown by the general formula (1) used in practical examples 1 ~ 3 with the composition ratio shown in table 1 and hardening material was obtained by the method similar to practical example 1. However, in comparative example 3, 1.0 g of di iso propyl peroxy di carbonate was used instead of 250 mg of 2, 2' - azo bis (2, 4 - di methyl valeronitrile) used as radical polymerization initiator.

**Table 1**

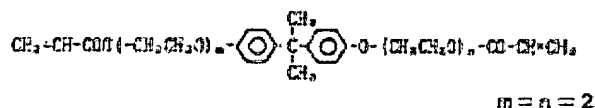
|                     | Polymerizable monomer of formula (1) (X) | Other vinyl group monomer (Y) | Mixing weight ratio (X/Y) | Refractive index | Permeability (%) | Tg (°C) | Water absorbance (%) |
|---------------------|--|-------------------------------|---------------------------|------------------|------------------|---------|----------------------|
| Practical example 1 | A  | -                             | 100/0                     | 1.656            | 87               | 115     | 0.30                 |
| 2                   | B  | -                             | 100/0                     | 1.650            | 87               | 110     | 0.30                 |
| 3                   | C  | -                             | 100/0                     | 1.648            | 87               | 107     | 0.31                 |
| 4                   | D  | -                             | 100/0                     | 1.650            | 87               | 115     | 0.23                 |
| 5                   | A  | Styrene                       | 15/85                     | 1.603            | 90               | 105     | 0.30                 |
| 6                   | A  | Methyl methacrylate           | 90/10                     | 1.637            | 89               | 112     | 0.40                 |

|                          |   |                        |       |       |    |     |      |
|--------------------------|---|------------------------|-------|-------|----|-----|------|
| 7                        | B | A-BPE <sup>1)</sup> -2 | 50/50 | 1.614 | 90 | 119 | 0.33 |
| 8                        | C | A-BPE <sup>2)</sup> -4 | 30/70 | 1.590 | 90 | 102 | 0.34 |
| 9                        | C | Di vinyl<br>benzene    | 70/30 | 1.629 | 89 | 125 | 0.32 |
| Comparative<br>example 1 | A | Methyl<br>methacrylate | 8/92  | 1.504 | 92 | 103 | 0.90 |
| 2                        | - | Methyl<br>methacrylate | 0/100 | 1.490 | 92 | 100 | 1.05 |
| 3                        | - | CR <sup>3)</sup> -39   | 0/100 | 1.499 | 92 | 90  | 1.30 |

1)



2)



3) Di ethylene glycol bis allyl carbonate

As is clear from table 1, hardened material obtained by hardening the hardening composite of the present invention has high refractive index and low water absorbance as compared to hardened material obtained in comparative examples 1 ~ 3.

#### [Effect / result of the invention]

The hardening composite of the present invention not only has excellent hardening property, but the hardened material obtained by hardening the hardening composite of the present invention has excellent optical evenness, high refractive index and high heat resistance and low water absorbance etc. due to which it is useful in industrial fields such as optical material, coating agent, sealing agent, paint, adhesive etc.

Patent Applicant

Showa Denko Kabushiki Kaisha  
(Showa Electrical Co. Ltd.)

Representative Patent Attorney Kikuchi Seiichi